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(54) Title: AMMONIA-FREE LATEX COMPOSITIONS

(57) Abstract: Provided herein are compositions comprising a stabilized, ammonia-free latex; a coagulation accelerant; a vulcanizing agent; and optionally a film forming agent. Preferably, the coagulation accelerant is morpholine. Also provided herein is a method of producing a formed article, the method comprising (a) optionally, a preheating step wherein a mold is heated at an elevated temperature; (b) a coagulant application step wherein a coagulant composition is applied to a mold; (c) an immersion step wherein a mold is immersed in a bath comprising a dip-molding composition as described herein; (d) a vulcanization step wherein the mold is exposed to an elevated temperature and/or ultraviolet radiation; (e) a demolding step wherein the formed article is separated from the mold; and (f) a washing step wherein the demolded article is washed.



Description

Title of Invention: AMMONIA-FREE LATEX COMPOSITIONS

BACKGROUND

- [0001] This application claims the benefit of priority from U.S. Provisional Application No. 63/563,752 filed on March 11, 2024 and U.S. Provisional Application No. 63/751,550 filed on January 30, 2025, the entire disclosures of which are incorporated herein by reference.
- [0002] Ammonia is a key ingredient in conventional latex rubber compositions. For example, when processing the latex that is extracted from the tree, small amounts of ammonia are typically added to inhibit coagulation as the latex is transported to the processing facility. In addition to ammonia, a biocide is conventionally used to preserve the latex to inhibit bacterial action and decomposition. Conventionally, high amounts of ammonia (~4% by weight) and low amounts of biocide (~1%), or low amounts of ammonia (~1%) and high amounts of biocide (~4%) are required.
- [0003] Once the latex is processed, the waste product residue, which is approximately 65% of the extracted material, is typically discarded. In conventional processes, the discarded residue is contaminated with ammonia and biocide and is therefore not environmentally friendly; the ammonia acts as a fertilizer, causing undesirable growth of plants and algae, and the biocide kills desirable microorganisms and microfauna. Some countries require costly treatments of the residues to reduce the amount of ammonia that is discarded into the environment. These treatments consume high quantities of water. The biocides used to complement traditional preservation treatments may also generate high levels of environmental contamination.
- [0004] Additionally, the added ammonia breaks down the proteins contained in the latex. This makes the resulting products, such as rubber gloves and condoms, allergenic for approximately 2% of the global population. In addition, ammonia generates nitrosamines within the material that are carcinogenic. Finally, because of the ammonia, the resulting rubber material has a strong odor that makes it unattractive for applications such as sports shoes, despite its superior mechanical properties. For these applications, the current alternative is to use natural rubber without ammonia, which also results in a rubber with a bad odor due to decomposition. Furthermore, this material requires large quantities of water to be processed.
- [0005] In addition, ammonia vapor affects the health of people throughout the material generation and manufacturing chain, from the farmer to the worker in the processing plant.
- [0006] As described in PCT Application No. PCT/IB2023/000064, the entire disclosure of which is incorporated herein by reference, the present inventors have developed

various methods of processing natural latex without the use of ammonia. For example, the ammonia-free methods described by the present inventors do not require exposing workers to ammonia liquid or vapor, and are therefore much less hazardous to the health of persons involved in the production, treatment, and handling of natural rubber. Additionally, the waste products of the ammonia-free process are significantly less harmful to the environment than the byproducts of traditional ammonia-based processing.

[0007] Despite the advantages of the ammonia-free methods described above, it has proven difficult to formulate ammonia-free latex rubber compositions for use in connection with certain manufacturing processes. Specifically, it has proven challenging to formulate ammonia-free latex rubber compositions for use in connection with dip molding applications.

[0008] There is therefore a need in the art for ammonia-free latex rubber compositions that are suitable for use in dip molding applications.

SUMMARY

[0009] Provided herein is a composition useful in dip-molding applications (referred to herein as a “dip-molding composition”) comprising a stabilized, ammonia-free latex; a coagulation accelerant; a vulcanizing agent; and optionally a film forming agent. Preferably, the coagulation accelerant is morpholine. Although the composition is referred to herein as a “dip-molding composition,” an important aspect of the present disclosure is directed to the provided compositions *per se*, and is not necessarily limited to the use of the provided compositions in dip-molding applications. For example, the provided compositions may also be used to create latex-based foams that are useful in the production of mattresses and similar items. In another example, the provided compositions may also be used to create casted items such as shoe soles and other thick rubber items.

[0010] In another aspect, provided herein is a method of producing a formed article, the method comprising (a) optionally, a preheating step wherein a mold is heated at an elevated temperature; (b) a coagulant application step wherein a coagulant composition is applied to a mold; (c) an immersion step wherein a mold is immersed in a bath comprising a dip-molding composition as described herein; (d) a vulcanization step wherein the mold is exposed to an elevated temperature and/or ultraviolet radiation; (e) a demolding step wherein the formed article is separated from the mold; and (f) optionally, a washing step.

[0011] Also provided herein is a formed article comprising ammonia-free latex, which may be produced by a method as provided herein. Non-limiting examples of formed articles

that may be produced using the provided methods include elastomeric films, gloves, balloons and condoms.

[0012] Other objects and features of the invention will be in part apparent and in part pointed out hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] [Fig.1] depicts a dip-molding process for forming tubular membranes, as generally described in Examples 1–14.

[0014] [Fig.2] is a photograph of a formed rubber glove on a mold (left image) and the same rubber glove following removal from the mold (right image), prepared using the dip-molding composition described in Example 1.

[0015] [Fig.3] is a photograph of a formed rubber glove on the mold (left image) and the same rubber glove following removal from the mold (right image), prepared using the dip-molding composition described in Example 7.

[0016] [Fig.4] is a graph that depicts the maximum stresses in MPa when applying a 30% deformation to ammonia-free latex samples prepared as described in Example 10 (0% calcium carbonate), Example 11 (1% calcium carbonate), Example 12 (2% calcium carbonate), and Example 13 (3% calcium carbonate).

[0017] [Fig.5] represents the minimum normalized relaxation percentage after a 10 minute test when applying a 30% deformation to ammonia-free latex prepared as described in Example 10 (0% calcium carbonate), Example 11 (1% calcium carbonate), Example 12 (2% calcium carbonate), and Example 13 (3% calcium carbonate).

DETAILED DESCRIPTION

[0018] Provided herein are ammonia-free compositions comprising natural rubber, also referred to as latex, that are suitable for use in processes for manufacturing dipped articles, also referred to as dip molding processes. For example, the ammonia-free compositions provided herein are useful to produce dipped articles such as gloves, balloons and condoms. Also provided herein are methods of forming products comprising latex, including elastomeric films, gloves, balloons and condoms, using the compositions provided herein.

[0019] In general, dip molding processes comprise an immersion step wherein a mold is immersed into a coagulant composition, followed by a dipping step wherein the mold is dipped into a product-specific formulation (e.g., a formulation comprising natural rubber latex). In conventional dip molding applications that utilize an ammoniated liquid natural rubber latex, the coagulant is typically composed of acetic acid, ethanol and calcium chloride or calcium nitrate. Conventional, ammoniated latex formulations typically have an alkaline pH of about 8.5 and often contain additives such as potassium hydroxide, potassium oleate, zinc diethyldithiocarbamate, zinc

dibutyldithiocarbamate, zinc oxide, antioxidants, and accelerants such as WINGSTAY L. Many of these chemicals are known to be harmful to both people and the environment.

[0020] As described in further detail below, the ammonia-free latex compositions provided herein are significantly different from the conventional, ammoniated formulations currently used in the dip molding industry. For example, the ammonia-free formulations provided herein may comprise an acidic latex composition having a pH between about 3 and about 5. Additionally, the ammonia-free formulations provided herein may be substantially free of additives that are harmful to people and/or to the environment, or may contain such additives in significantly lower quantities than the additives present in conventional, ammoniated latex formulations.

[0021] The ammonia-free methods described herein provide several advantages over traditional latex processing methods. For example, the methods described herein do not require exposing workers to ammonia liquid or vapor, and are therefore much less hazardous to the health of persons involved in the production, treatment, and handling of natural rubber. Additionally, the waste products of the present process are ammonia-free, and therefore are significantly less harmful to the environment than the byproducts of traditional ammonia-based processing, and don't contain pesticides, biocides or microbicides.

[0022] In preferred embodiments, the methods described herein may produce liquid latex having a shelf life of a year or longer (e.g., at least two years, at least three years, or even longer), which is significantly longer than traditional ammonia-treated liquid latex. As used herein, the term "shelf life" refers to the period of time for which a product may be stored under ambient conditions (i.e., in the absence of refrigeration or freezing) without exhibiting significant degradation or change in its physical or chemical properties.

[0023] Likewise, products produced using the ammonia-free rubber compositions described herein exhibit several advantages over otherwise similar products produced using conventional, ammonia-treated rubber. For example, the methods described herein produce a liquid latex composition that is non-allergenic (due to the absence of added ammonia). Latex products produced according to the methods described herein do not exhibit the strong odors characteristic of added ammonia, making them more attractive for use in consumer-facing applications such as athletic footwear. Additionally, ammonia-free rubber products produced according to the methods described herein are purer and exhibit a clearer color than products produced using traditional ammonia-treated rubber, which may be viewed favorably by consumers of gloves, condoms, and medical devices, among others. Moreover, products produced using the

ammonia-free rubber have superior physicochemical characteristics compared with traditional, ammonia-treated rubber products.

Dip-Molding Compositions

[0024] The dip-molding compositions provided herein may comprise one or more of (1) a stabilized, ammonia-free latex composition; (2) an accelerant; (3) a vulcanizing agent; and (4) a film forming agent. These components are described in further detail below. Optionally, the dip molding composition may comprise one or more additional components. For example, the dip molding composition may be an aqueous composition that further comprises water.

[0025] The dip-molding composition preferably has a pH of between about 5 and about 8, and more preferably between about 6 and about 7. The dip-molding composition may, for example, have a pH of at least about 6, at least about 6.1, at least about 6.2, at least about 6.3, or at least about 6.4. Conversely, the dip-molding composition may, for example, have a pH of no greater than about 7, no greater than about 6.9, no greater than about 6.8, no greater than about 6.7, or no greater than about 6.6. The dip-molding composition may have a pH that falls within a range bounded by any minimum value and any maximum value provided above. As a non-limiting example, the dip-molding composition may have a pH of from about 6.3 to about 6.8. In a particularly preferred embodiment, the dip-molding composition has a pH of about 6.4.

Stabilized, Ammonia-Free Latex Composition

[0026] The dip-molding composition may comprise a stabilized, ammonia-free latex composition. The stabilized, ammonia-free latex composition may comprise one or more of: latex, a stabilizing agent, a preserving agent, and a pH adjustment agent.

[0027] For example, the stabilized, ammonia-free latex composition may comprise a stabilizing agent. The stabilizing agent may comprise a surfactant. The surfactant may be, for example, an anionic or nonionic surfactant. For example, the stabilizing agent may comprise one or more surfactants selected from the group consisting of alkylbenzene sulfonates, fatty acid alcohols, and ethoxylated fatty acid alcohols. Advantageously, the stabilizing agent does not comprise ammonia.

[0028] Non-limiting examples of suitable stabilizing agents include methanesulfonic acid, paratoluene sulfonic acid, 2-sulfoacetic acid, 2-naphthalensulfonic acid, 2-anthracenesulfonic acid, p-methylbenzenesulfonic acid, 4-amino-2,3-dichlorobenzenesulfonic acid, benzenesulfonic acid, 1-phenanthanesulfonic acid, phenolsulfonic acid, ethanesulfonic acid, propanesulfonic acid, butanesulfonic acid, pentanesulfonic acid, hexanesulfonic acid, heptanesulfonic acid, octanesulfonic acid, nonanesulfonic acid, decanosulfonic acid, isopropanesulfonic acid, terbutanesulfonic acid, benzenesulfonic acid, ortho-toluenesulfonic acid, dodecylbenzene sulfonic acid, methylbenzene

sulfonic acid, tertbutyl sulfonic acid, propylbenzene sulfonic acid, methylbenzene sulfonic acid, ethylbenzene sulfonic acid, butylbenzene sulfonic acid, pentylbenzene sulfonic acid, hexylbenzene sulfonic acid, heptylbenzene sulfonic acid, octylbenzene sulfonic acid, nonylbenzene sulfonic acid, decabenzene sulfonic acid, undecabenzene sulfonic acid, trifluoromethanesulfonic acid, 10-camphorsulfonic acid, metasulfonic acid, xylenesulfonic acid, lauric alcohol, ethoxylated lauric alcohol, ethoxylated long chain alcohols having from 7 to 15 carbons, and mixtures or combinations thereof. Generally, the surfactant may be aqueous or anhydrous. For example, the stabilizing agent may comprise an ethoxylated lauric alcohol. As a further example, the stabilizing agent may comprise a dodecylbenzene sulfonic acid.

- [0029] The stabilized, ammonia-free latex composition may comprise a preserving agent. The preserving acts to preserve the latex and prevent its degradation by bacteria or other microorganisms or microfauna. Advantageously, the preserving agent does not comprise ammonia.
- [0030] The preserving agent may comprise an acid. For example, the preserving agent may comprise a halogenated acid. Non-limiting examples of suitable preserving agents include hydrochloric acid, hydrofluoric acid, iodic acid, and hydrobromic acid. Generally, the acid may be aqueous or anhydrous. For example, the preserving agent may comprise hydrofluoric acid.
- [0031] Without being bound to a particular theory, it is believed that addition of a halogenated acid acts to replace the hydrogen sulfide present in the cysteine of the peptides and/or proteins in natural latex sap, and that this process acts to preserve the natural latex in its liquid form and prevent degradation by microorganisms.
- [0032] The stabilized, ammonia-free latex composition may comprise a pH adjustment agent. The pH adjustment agent may be used, if necessary, to increase the pH of the liquid latex composition to a range of from about 6 to about 10, which is optimal for the storage stability of the composition. Non-limiting examples of suitable pH adjustment agents include sodium hydroxide, potassium hydroxide, amines, and mixtures or combinations thereof.
- [0033] Non-limiting examples of stabilized, ammonia-free latex compositions include those provided in PCT Application No. PCT/IB2023/000064, the entire disclosure of which is incorporated herein by reference. An illustrative list of stabilized, ammonia-free latex compositions is provided in Table 1 below.
- [0034] **Table 1: Stabilized Ammonia-Free Latex Compositions**

Formulation Name	Composition
AFLATEX ALFA	<ul style="list-style-type: none"> • 98.6 volume % of filtered raw latex • 1.0 volume % of ethoxylated lauric alcohol (7 EO) • 0.4 volume % of a mixture of 50% hydrofluoric acid and 50% water.
AFLATEX DELTA	<ul style="list-style-type: none"> • 98.6 volume % of filtered raw latex • 1.0 volume % of a mixture of 50% ethoxylated lauric alcohol (3 EO) and 50% ethoxylated lauric alcohol (7 EO) (overall average of 5 EO) • 0.4 volume % of a mixture of 50% hydrofluoric acid and 50% water
AFLATEX GAMMA	<ul style="list-style-type: none"> • 98.6 volume % of filtered raw latex • 1.0 volume % of ethoxylated lauric alcohol (9 EO) • 0.4 volume % of a mixture of 50% hydrofluoric acid and 50% water
AFLATEX OMEGA	<ul style="list-style-type: none"> • 98.6 volume % of filtered raw latex • 1.0 volume % of ethoxylated lauric alcohol (10 EO) • 0.4 volume % of a mixture of 50% hydrofluoric acid and 50% water
AFLATEX EPSILON	<ul style="list-style-type: none"> • 98.6 volume % of filtered raw latex • 1.0 volume % of ethoxylated lauric alcohol (12 EO) • 0.4 volume % of a mixture of 50% hydrofluoric acid and 50% water
AFLATEX THETA	<ul style="list-style-type: none"> • 98.6 volume % of filtered raw latex • 1.0 volume % of ethoxylated lauric alcohol (18 EO) • 0.4 volume % of a mixture of 50% hydrofluoric acid and 50% water
AFLATEX BETA	<ul style="list-style-type: none"> • 98.0 volume % of filtered raw latex • 2.0 volume % of linear dodecylbenzene sulfonic acid

[0035] The dip-molding composition may comprise a stabilized, ammonia-free latex composition in a concentration of at least about 40% by weight, at least about 50% by weight, at least about 60% by weight, or at least about 70% by weight of the composition as a whole. Typically, the dip-molding composition comprises a stabilized, ammonia-free latex compositions in a concentration of no greater than about 95%, no greater than about 90%, no greater than about 80%, or no greater than 75% of the

composition as a whole. For example, the dip-molding composition may comprise a stabilized, ammonia-free latex composition in a concentration that falls within a range bounded by a minimum value and a maximum value provided above. As a non-limiting example, the dip-molding composition may comprise a stabilized, ammonia-free latex composition in a concentration of from about 60% by weight to about 90% by weight of the composition as a whole.

Accelerant

[0036] The dip-molding composition may comprise a vulcanization accelerant (also referred to herein as simply an “accelerant”). Preferably, the accelerant comprises morpholine.

[0037] The dip-molding composition may comprise an accelerant in a concentration of, for example, at least about 0.05% by weight, at least about 0.1% by weight, at least about 0.2% by weight, or at least about 0.3% by weight of the composition as a whole. Typically, the dip-molding composition comprises an accelerant in a concentration of, for example, no greater than about 5%, no greater than about 2%, no greater than about 1%, or no greater than 0.5% of the composition as a whole. The dip-molding composition may comprise an accelerant in a concentration that falls within a range bounded by any minimum value and any maximum value provided above. As a non-limiting example, the dip-molding composition may comprise an accelerant in a concentration of from about 0.1% by weight to about 0.5% by weight of the composition as a whole. In a non-limiting example the accelerant is added to the dipping formulation until a pH of at least 5.5 is reached, at least 6.5, at least 7.5, or at least 8.5 is reached.

Vulcanizing Agent

[0038] The dip-molding composition may comprise a vulcanizing agent. For example, the vulcanizing agent may comprise sulfur. The sulfur may be dispersed in water, or a mixture of water and linear dodecylbenzene sulfonic acid (DBS), or serum resulting from the centrifuged latex.

[0039] The dip-molding composition may comprise a vulcanizing agent in a concentration of at least about 0.1% by weight, at least about 1% by weight, at least about 2% by weight, or at least about 3% by weight of the composition as a whole. Typically, the dip-molding composition comprises a vulcanizing agent in a concentration of no greater than about 10%, or no greater than about 5% of the composition as a whole. For example, the dip-molding composition may comprise a vulcanizing agent in a concentration that falls within a range bounded by a minimum value and a maximum value provided above. As a non-limiting example, the dip-molding composition may comprise a vulcanizing agent in a concentration of from about 1% by weight to about 2% by weight of the composition as a whole.

Film-Forming Agent

[0040] The dip-molding composition may comprise a film-forming agent. Non-limiting examples of suitable film-forming agents include hydroxyethyl cellulose, carboxymethyl cellulose, and collagen.

[0041] The dip-molding composition may comprise a film-forming agent in a concentration of at least about 0.1% by weight, at least about 0.2% by weight, at least about 0.3% by weight, or at least about 0.4% by weight of the composition as a whole. Typically, the dip-molding composition comprises a film-forming agent in a concentration of no greater than about 5%, no greater than about 2%, no greater than about 1%, or no greater than 0.8% of the composition as a whole. For example, the dip-molding composition may comprise a film-forming agent in a concentration that falls within a range bounded by a minimum value and a maximum value provided above. As a non-limiting example, the dip-molding composition may comprise a film-forming agent in a concentration of from about 0.1% by weight to about 1% by weight of the composition as a whole.

Filler

[0042] The dip-molding composition may comprise a filler. A non-limiting example of a suitable filler is calcium carbonate or silicon dioxide in a concentration of at least about 0.1% by weight, at least about 1% by weight, at least about 5% by weight, or at least about 10% by weight of the composition as a whole. Typically, the dip-molding composition comprises a filler in a concentration of no greater than about 20%, or no greater than about 15% of the composition as a whole.

Water

[0043] The dip-molding composition may be an aqueous composition that further comprises water. In general, water may be present in an amount that accounts for the balance of the composition, in combination with the components discussed above. As a non-limiting example, the dip molding composition may comprise water in a concentration of from about 20% to about 50% by weight of the composition as a whole.

Methods for Preparing Formed Articles

[0044] Provided herein are methods for preparing formed articles utilizing a dip-molding composition as described herein. The methods may comprise one or more of the following steps: (a) a preheating step wherein a mold is heated at an elevated temperature; (b) a coagulant application step wherein a coagulant composition is applied to a mold; (c) an immersion step wherein a mold is immersed in a bath comprising a dip-molding composition; (d) a vulcanization step wherein the mold is exposed to an elevated temperature; and (e) a demolding step wherein the formed article is separated from the mold. These steps are described in further detail below.

Preheating Step

- [0045] The method may comprise a preheating step wherein a mold is heated at an elevated temperature. Alternately, the mold may be kept at room temperature before coagulant application and immersion steps.
- [0046] The mold may be heated, for example, at a temperature of at least about 50#°C, at least about 60#°C, at least about 70#°C, at least about 80#°C, or at least about 90#°C. Typically, the mold is heated at a temperature of no greater than about 120#°C, no greater than about 110#°C, no greater than about 100#°C, or no greater than about 90#°C. For example, the mold may be heated at a temperature that falls within a range bounded by a minimum value and a maximum value provided above. As a non-limiting example, the mold may be heated at a temperature of from about 80#°C to about 100#°C.
- [0047] The mold may be heated, for example, for a period of at least about 1 minute, at least about 2 minutes, at least about 5 minutes, or at least about 10 minutes. Typically, the mold is heated for a period of no longer than about 30 minutes.

Coagulant Application Step

- [0048] The method may comprise a coagulant application step wherein a coagulant composition is applied to a mold. For example, the mold may be immersed in a bath comprising the coagulant composition.
- [0049] The coagulant composition comprises at least one coagulating agent. The coagulating agent, acts to coagulate the liquid latex, thereby producing a solid latex composition.
- [0050] The coagulant composition may comprise an alcohol. For example, the coagulant composition may comprise a C₁ to C₈ alcohol, more preferably a C₁ to C₆ alcohol. Non-limiting examples of suitable coagulating agents include methanol, ethanol, n-propanol, benzyl alcohol, isopropyl alcohol, isobutyl alcohol, tertiary butyl alcohol, pentanol, hexanol, heptanol, octanol, and mixtures or combinations thereof. Generally, the alcohol may be aqueous or anhydrous. For example, the coagulating agent may comprise ethanol.
- [0051] The coagulant composition may comprise an acid. For example, the coagulant composition may comprise an organic acid. A non-limiting example of a suitable organic acid is acetic acid or a linear dodecylbenzene sulfonic acid (DBS).
- [0052] The coagulant composition may comprise a salt, which is preferably a calcium salt. For example, the coagulant composition may comprise calcium chloride, calcium nitrate, calcium carbonate or a combination thereof.
- [0053] The mold may immersed in a bath comprising the coagulant composition, for example, for a period of at least about 1 second, at least about 2 seconds, at least about 5 seconds, at least about 10 seconds, or at least about 15 seconds or more. Typically,

the mold is immersed in a bath comprising the coagulant composition for a period of no longer than about 1 minute.

Immersion Step

[0054] The method may comprise an immersion step wherein a mold is immersed in a bath comprising a dip-molding composition, which may be selected as described in detail above.

[0055] The mold may be immersed in a bath comprising the dip-molding composition, for example, for a period of at least about 10 seconds, at least about 20 seconds, at least about 30 seconds, at least about 45 seconds, or at least about 1 minute or more. Typically, the mold is immersed in a bath comprising the dip-molding composition for a period of no longer than about 5 minutes.

Drying Step

[0056] The method may optionally comprise a drying step. The drying step may be performed at relatively low temperatures, for example, from room temperature (e.g., 25#°C) to about 50#°C. Drying times typically vary from about 30 minutes to about 45 minutes when conducted at elevated temperatures of from about 50#°C to about 60#°C. Alternatively, the drying step may comprise blow drying with fans for a period of from about 2 hours to about 4 hours at room temperature.

Vulcanization Step at an Elevated Temperature

[0057] The method may comprise a vulcanization step wherein the mold is heated at an elevated temperature.

[0058] The mold may be heated, for example, at a temperature of at least about 50#°C, at least about 60#°C, at least about 70#°C, at least about 80#°C, or at least about 90#°C. Typically, the mold is heated at a temperature of no greater than about 120#°C, no greater than about 110#°C, no greater than about 100#°C, or no greater than about 90#°C. For example, the mold may be heated at a temperature that falls within a range bounded by a minimum value and a maximum value provided above. As a non-limiting example, the mold may be heated at a temperature of from about 80#°C to about 100#°C.

[0059] The mold may be heated, for example, for a period of at least about 1 minute, at least about 5 minutes, at least about 10 minutes, at least about 15 minutes, or at least about 30 minutes. Typically, the mold is heated for a period of no longer than about 2 hours, and more typically for no longer than about 1 hour, or no longer than about 45 minutes.

Vulcanization Step Using Ultraviolet Rays

[0060] The method may comprise a vulcanization step wherein the mold is irradiated with ultraviolet (UV) radiation. For example, the vulcanization step may comprise ir-

radiating the mold with radiation having a wavelength of from about 100 nm to about 400 nm. As a non-limiting example, the vulcanization step may comprise irradiating the mold with radiation having a wavelength of from about 350 nm to about 380 nm (for example, about 365 nm).

- [0061] Preferably, the mold is irradiated for a time sufficient to impart at least about 200 J/cm² to the surface of the mold. For example, the mold may be irradiated for a time sufficient to impart at least about 250 J/cm², at least about 300 J/cm², at least about 350 J/cm², or at least about 400 J/cm² to the surface of the mold. Conversely, imparting more energy than is needed to ensure vulcanization is generally not helpful, and in some cases can even lead to degradation of the mold. Accordingly, the mold is typically irradiated for a time sufficient to impart at most about 800 J/cm² at most about 700 J/cm², at most about 600 J/cm², or at most about 500 J/cm² to the surface of the mold.

Demolding Step

- [0062] The method may comprise a demolding step wherein the formed article is separated from the mold.

Washing Step

- [0063] The method may comprise one or more washing steps wherein the formed article that has been separated from the mold is washed using a washing composition.
- [0064] Each washing step may be carried out for a period of, for example, at least about 5 minutes, at least about 10 minutes, at least about 20 minutes, at least about 30 minutes, or at least about 45 minutes. Typically, each washing step is carried out for a period of no longer than about 3 hours, and more typically for no longer than about 2 hours, or no longer than about 1 hour.
- [0065] For example, the method may comprise a washing step wherein the formed article is washed using a washing composition comprising linear dodecylbenzene sulfonic acid (DBS). The washing composition may be prepared, for example, by diluting DBS with water. The washing composition may comprise DBS in a concentration of, for example, at least about 0.1% by weight, at least about 1% by weight, at least about 5% by weight, or at least about 10% by weight of the composition as a whole. Typically, the composition comprises DBS in a concentration of no greater than about 40%, no greater than about 30%, no greater than about 20%, or no greater than 15% of the composition as a whole.
- [0066] As a further example, the method may comprise a washing step wherein the formed article is washed using a washing composition comprising calcium hypochlorite. The washing composition may be prepared, for example, by diluting calcium hypochlorite with water. The washing composition may be prepared, for example, by diluting

calcium hypochlorite with water. The washing composition may comprise calcium hypochlorite in a concentration of, for example, at least about 0.1% by weight, at least about 1% by weight, at least about 5% by weight, or at least about 10% by weight of the composition as a whole. Typically, the composition comprises calcium hypochlorite in a concentration of no greater than about 40%, no greater than about 30%, no greater than about 20%, or no greater than 15% of the composition as a whole.

[0067] As a further example, the method may comprise a washing step wherein the formed article is washed using a washing composition comprising hypochlorous acid. The washing composition may be prepared, for example, by diluting hypochlorous acid with water. The washing composition may comprise hypochlorous acid in a concentration of, for example, at least about 0.1% by weight, at least about 1% by weight, at least about 5% by weight, or at least about 10% by weight of the composition as a whole. Typically, the composition comprises hypochlorous acid in a concentration of no greater than about 40%, no greater than about 30%, no greater than about 20%, or no greater than 15% of the composition as a whole.

[0068] In a preferred embodiment, the method comprises a first washing step wherein the formed article is washed using a first washing composition comprising DBS, and a second washing step wherein the formed article is washed using a second washing composition comprising calcium hypochlorite, hypochlorous acid, or a mixture thereof.

Formed Article

[0069] Also provided herein is a formed article comprising ammonia-free latex. In some embodiments, the formed article is produced by a method as described above.

[0070] For example, the formed article may comprise a stabilized, ammonia-free latex composition which may be selected as described above.

[0071] As described above, ammonia-free solid rubber produced using the methods provided herein exhibit a significant improvement in mechanical properties. These increases in mechanical properties can lead to material reduction during manufacture, which not only reduces cost but also results in lighter products. This is particularly advantageous in applications such as the manufacturing of gloves, condoms, and athletic shoes, where strong and lightweight materials are highly desirable.

EXAMPLES

[0072] The following non-limiting examples are provided to further illustrate the present disclosure.

[0073] Dip-Molding Process for Preparing Rubber Gloves Using a Heated Mold

[0074] Nine different ammonia-free dip-molding compositions, described below as Examples 1 through 9, were prepared and used to manufacture miniature gloves and

tubular membranes. A schematic diagram of the glove and tubular membrane dipping manufacturing processes is depicted in [Fig.1].

[0075] The following steps were followed in the glove and tubular membrane dipping manufacturing processes:

[0076] Step 1: The molds were preheated in an oven for a period of 10 minutes at 90#°C to simulate a continuous manufacturing process such as depicted in [Fig.1].

[0077] Step 2: The molds were immersed in a coagulant bath. The total immersion time was 25 seconds, which included 10 seconds insertion into the coagulant, 5 seconds resting inside the coagulant and 10 seconds pulling the mold from the coagulant. The coagulant bath was composed of a third of ethanol with a 95% concentration, a third of 5 % concentration acetic acid (commercial vinegar) and a third of a 10% calcium chloride concentration in distilled water.

[0078] Step 3: After immersion in the coagulant, the mold was immersed in the latex for a total immersion time of 85 seconds, which included 13.5 seconds of insertion into the latex, 58 seconds resting inside the latex and 13.5 seconds of pulling the mold from the latex.

[0079] Step 4: The latex covered molds were inserted in an oven at 90#°C for a 30 minute vulcanization process.

[0080] Step 5: The molds were allowed to cool and the membrane products were demolded, as shown in [Fig.2].

[0081] Step 6: The demolded products were washed for 30 minutes using a first washing composition comprising DBS in a concentration of 5% by weight, and were subsequently washed for 30 minutes using a second washing composition comprising hypochlorous acid in a concentration of 3% by weight.

[0082] The process steps described above were used to prepare molded articles using a variety of dip-molding compositions, as described in detail in Examples 1–9 below.

[0083] Example 1: Dipping with AFLATEX ALFA with chemicals diluted in distilled water

[0084] A dipping formulation was prepared by combining: 100 grams of centrifuged stabilized and preserved AFLATEX ALFA liquid latex composition with a dry rubber content of 60%, 0.7 grams of sulfur diluted in 20 grams of distilled water and 0.21 grams of ethoxylated lauric alcohol (7 moles), 0.55 grams of collagen diluted in 20 grams of distilled water and 0.44 grams of a 99% concentration morpholine solution. The morpholine solution was added until a pH of 6.4 was reached.

Example 2: Dipping with pigmented AFLATEX ALFA

[0085] A dipping formulation was prepared with the same chemicals and proportions as in example 1, with the addition of 0.7 grams of green aniline dye diluted in 10 grams of distilled water.

[0086] Example 3: Dipping with AFLATEX ALFA with chemicals diluted in serum recovered from centrifuging process

[0087] A dipping formulation was prepared with the same chemicals and proportions as in Example 1, except that sulfur and collagen were diluted in the serum recovered from centrifuging the latex instead of distilled water.

[0088] Example 4: Dipping with AFLATEX BETA with chemicals diluted in distilled water

[0089] A dipping formulation was prepared by combining: 100 grams of centrifuged stabilized and preserved AFLATEX BETA liquid latex composition with a dry rubber content of 60%, 0.7 grams of sulfur diluted in 20 grams of distilled water and 0.21 grams of ethoxylated lauric alcohol (7 moles), 0.55 grams of collagen diluted in 20 grams of distilled water and 0.48 grams of a 99% concentration morpholine solution. The morpholine solution was added until a pH of 5.7 was reached.

Example 5: Dipping with pigmented AFLATEX BETA

[0090] A dipping formulation was prepared with the same chemicals and proportions as in Example 4, with the addition of 0.7 grams of green aniline dye diluted in 10 grams of distilled water.

[0091] Example 6: Dipping with AFLATEX BETA with chemicals diluted in serum recovered from centrifuging process

[0092] A dipping formulation was prepared with the same chemicals and proportions as in Example 4, except that sulfur and collagen were diluted in the serum recovered from centrifuging the latex instead of distilled water.

[0093] Example 7: Dipping with AFLATEX BETA after heating such AFLATEX BETA and combining with chemicals diluted in distilled water

[0094] Heating AFLATEX BETA to 70#°C, and preparing a dipping formulation by combining: 100 grams of centrifuged stabilized, preserved and heated AFLATEX BETA liquid latex with a dry rubber content of 60%, 1.75 grams of sulfur diluted in 20 grams of distilled water and 0.21 grams of ethoxylated lauric alcohol (7 moles), 0.55 grams of collagen diluted in 20 grams of distilled water and 0.48 grams of a 99% concentration morpholine solution. The morpholine solution was added until a pH between 6 and 7 was reached.

[0095] Example 8: Dipping with pigmented heated AFLATEX BETA

[0096] A dipping formulation was prepared with the same chemicals and proportions as in example 7, with the addition of 0.7 grams of green aniline dye diluted in 10 grams of distilled water.

[0097] Example 9: Dipping with AFLATEX BETA after heating such AFLATEX BETA and with chemicals diluted in serum recovered from centrifuging process

- [0098] A dipping formulation was prepared with the same chemicals and proportions as in Example 7, except that sulfur and collagen were diluted in the serum recovered from centrifuging the latex instead of distilled water.
- [0099] Dip-Molding Process for Preparing Rubber Gloves Using UV curing
- [0100] Four different ammonia-free dip-molding compositions, described below as Examples 10–13, were prepared and used to manufacture miniature gloves and tubular membranes. A schematic diagram of the glove and tubular membrane dipping manufacturing processes is depicted in [Fig.1].
- [0101] The following steps were followed in the glove and tubular membrane dipping manufacturing processes:
- [0102] Step 1: The molds were preheated in an oven for a period of 10 minutes at 90#°C to simulate a continuous manufacturing process such as depicted in [Fig.1].
- [0103] Step 2: The molds were immersed in a coagulant bath. The total immersion time was 25 seconds, which included 10 seconds insertion into the coagulant, 5 seconds resting inside the coagulant and 10 seconds pulling the mold from the coagulant. The coagulant bath was composed of 74.9%W/V of ethanol with a 95% concentration, 25%/W/V of calcium chloride and 0.1%W/V of DBS.
- [0104] Step 3: After immersion in the coagulant, the mold was immersed in the latex for a total immersion time of 85 seconds, which included 13.5 seconds of insertion into the latex, 58 seconds resting inside the latex and 13.5 seconds of pulling the mold from the latex.
- [0105] Step 4: The latex covered molds were set out to dry at room temperature.
- [0106] Step 5: The latex covered molds were inserted into UV irradiated chambers. The molds were exposed to UV radiation at an intensity of 26 mW/cm² for a total time of 2, 4, 6, or 8 hours as set forth in Table 2 below. For comparative purposes, a set of molds was also prepared without exposure to UV radiation.
- [0107] Step 6: The membrane products were demolded.
- [0108] Step 6: The demolded products were washed for 30 minutes using a first washing composition comprising DBS in a concentration of 5% by weight, and were subsequently washed for 30 minutes using a second washing composition comprising hypochlorous acid in a concentration of 3% by weight.
- [0109] The process steps described above were used to prepare molded articles using a variety of dip-molding compositions, as described in detail in Examples 10–13 below.
- [0110] Example 10: Dipping with AFLATEX BETA with chemicals diluted in distilled water
- [0111] A dipping formulation was prepared by combining: 100 grams of centrifuged stabilized and preserved AFLATEX BETA liquid latex composition with a dry rubber content of 60%, 1.75 grams of sulfur diluted in 1.75 grams of distilled water and 0.44

grams of DBS, and 0.44 grams of a 99% concentration morpholine solution. The morpholine solution was added until a pH of 5.5 was reached.

[0112] Example 11: Dipping with AFLATEX BETA with chemicals diluted in distilled water

[0113] A dipping formulation was prepared by combining: 100 grams of centrifuged stabilized and preserved AFLATEX BETA liquid latex composition with a dry rubber content of 60%, 1.75 grams of sulfur diluted in 1.75 grams of distilled water and 0.44 grams of DBS, and 0.44 grams of a 99% concentration morpholine solution. The morpholine solution was added until a pH of 5.5 was reached. Finally, 1 gram of calcium carbonate dissolved in 10 grams of water was added to the dipping formulation. A pH rise was observed with the addition of the calcium carbonate.

[0114] Example 12: Dipping with AFLATEX BETA with chemicals diluted in distilled water

[0115] A dipping formulation was prepared by combining: 100 grams of centrifuged stabilized and preserved AFLATEX BETA liquid latex composition with a dry rubber content of 60%, 1.75 grams of sulfur diluted in 1.75 grams of distilled water and 0.44 grams of DBS, and 0.44 grams of a 99% concentration morpholine solution. The morpholine solution was added until a pH of 5.5 was reached. Finally, 2 gram of calcium carbonate dissolved in 10 grams of water was added to the dipping formulation. A pH rise was observed with the addition of the calcium carbonate.

[0116] Example 13: Dipping with AFLATEX BETA with chemicals diluted in distilled water

[0117] A dipping formulation was prepared by combining: 100 grams of centrifuged stabilized and preserved AFLATEX BETA liquid latex composition with a dry rubber content of 60%, 1.75 grams of sulfur diluted in 1.75 grams of distilled water and 0.44 grams of DBS, and 0.44 grams of a 99% concentration morpholine solution. The morpholine solution was added until a pH of 5.5 was reached. Finally, 3 gram of calcium carbonate dissolved in 10 grams of water was added to the dipping formulation. A pH rise was observed with the addition of the calcium carbonate.

Stress and Relaxation Testing

[0118] Surprisingly, as shown in Table 2 below and as depicted in [Fig.4], it was observed that applying UV radiation increased the strength of the dipped membranes.

[0119] Additionally, as shown in Table 2 below and as depicted in [Fig.5], the UV-irradiated membranes exhibited significantly lower stress reduction during a 10 minute relaxation test. For example, the formulation with 1% calcium carbonate exhibited the highest stress of 0.312 MPa and only relaxed down to 96.44% after 10 minutes.

	Calcium Carbonate Addition (%)							
	Example 10 (0% CaCO ₃)		Example 11 (1% CaCO ₃)		Example 12 (2% CaCO ₃)		Example 13 (3% CaCO ₃)	
UV Curing Time (hr)	Maximum Stress (MPa)	Minimum Normalized Relaxation (%)	Maximum Stress (MPa)	Minimum Normalized Relaxation (%)	Maximum Stress (MPa)	Minimum Normalized Relaxation (%)	Maximum Stress (MPa)	% Minimum Normalized Relaxation
0	0.113	52.87%	0.048	10.42%	0.059	10.30%	0.056	13.48%
2	0.171	83.18%	0.146	81.32%	0.273	93.03%	0.275	92.67%
4	0.147	83.34%	0.312	96.44%	0.242	91.94%	0.257	91.75%
6	0.136	83.07%	0.277	95.51%	0.296	93.55%	0.263	92.45%
8	0.124	80.56%	0.267	92.09%	0.191	87.15%	0.140	86.68%

[0120] When introducing elements of the present disclosure or the preferred embodiment(s) thereof, the articles “a”, “an”, “the”, and “said” are intended to mean that there are one or more of the elements. The terms “comprising”, “including”, and “having” are intended to be inclusive and mean that there may be additional elements other than the listed elements.

[0121] In view of the above, it will be seen that the several objects of the disclosure are achieved and other advantageous results attained.

[0122] As various changes could be made in the above products and methods without departing from the scope of the disclosure, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

Claims

- [Claim 1] An ammonia-free latex composition comprising
- (a) a stabilized, ammonia-free latex;
 - (b) a coagulation accelerant comprising morpholine; and
 - (c) a vulcanizing agent.
- [Claim 2] The composition of claim 1 wherein the stabilized, ammonia-free latex comprises a surfactant selected from the group consisting of methanesulfonic acid, paratoluene sulfonic acid, 2-sulfoacetic acid, 2-naphthalensulfonic acid, 2-anthracensulfonic acid, p-methylbenzenesulfonic acid, 4-amino-2,3-dichlorobenzenesulfonic acid, benzenesulfonic acid, 1-phenanthanesulfonic acid, phenolsulfonic acid, ethanesulfonic acid, propanesulfonic acid, butanesulfonic acid, pentanesulfonic acid, hexanesulfonic acid, heptanesulfonic acid, octanesulfonic acid, nonanesulfonic acid, decanosulfonic acid, isopropanesulfonic acid, terbutanesulfonic acid, benzenesulfonic acid, ortho-toluenesulfonic acid, dodecylbenzene sulfonic acid, methylbenzene sulfonic acid, tertbutyl sulfonic acid, propylbenzene sulfonic acid, methylbenzene sulfonic acid, ethylbenzene sulfonic acid, butylbenzene sulfonic acid, pentylbenzene sulfonic acid, hexylbenzene sulfonic acid, heptylbenzene sulfonic acid, octylbenzene sulfonic acid, nonylbenzene sulfonic acid, decabenzene sulfonic acid, undecabenzene sulfonic acid, trifluoromethanesulfonic acid, 10-camphorsulfonic acid, metasulfonic acid, xylenesulfonic acid, lauric alcohol, ethoxylated lauric alcohol, ethoxylated long chain alcohols having from 7 to 15 carbons, and mixtures or combinations thereof.
- [Claim 3] The composition of claim 2 wherein the stabilized, ammonia-free latex comprises an ethoxylated lauric alcohol.
- [Claim 4] The composition of claim 2 wherein the stabilized, ammonia-free latex comprises dodecylbenzene sulfonic acid.
- [Claim 5] The composition of any one of claims 1 to 4 wherein the stabilized, ammonia-free latex comprises an acid.
- [Claim 6] The composition of claim 5 wherein the stabilized, ammonia-free latex comprises a halogenated acid.
- [Claim 7] The composition of claim 6 wherein the stabilized, ammonia-free latex comprises a halogenated acid selected from the group consisting of hydrochloric acid, hydrofluoric acid, iodic acid, and hydrobromic acid.

- [Claim 8] The composition of claim 7 wherein the stabilized, ammonia-free latex comprises hydrofluoric acid.
- [Claim 9] The composition of any one of claims 1 to 8 comprising the stabilized, ammonia-free latex in a concentration of at least about 60% by weight of the composition as a whole.
- [Claim 10] The composition of any one of claims 1 to 9 comprising morpholine in a concentration of from about 0.1% by weight to about 0.5% by weight of the composition as a whole.
- [Claim 11] The composition of any one of claims 1 to 10 wherein the vulcanizing agent comprises sulfur.
- [Claim 12] The composition of any one of claims 1 to 11 comprising the vulcanizing agent in a concentration of from about 0.1% by weight to about 1% by weight of the composition as a whole.
- [Claim 13] The composition of any one of claims 1 to 12 wherein the composition further comprises a film-forming agent selected from the group consisting of hydroxyethyl cellulose, carboxymethyl cellulose, collagen, and combinations thereof.
- [Claim 14] The composition of any one of claims 1 to 13 comprising the film-forming agent in a concentration of from about 0.1% by weight to about 1% by weight of the composition as a whole.
- [Claim 15] The composition of any one of claims 1 to 14 wherein the composition further comprises water.
- [Claim 16] The composition of any one of claims 1 to 15 comprising filler in a concentration of from about 0.1% by weight to about 10% by weight of the composition as a whole.
- [Claim 17] An ammonia-free latex foam comprising:
(a) the composition of any one of claims 1 to 16; and
(b) a gas dispersed within said composition.
- [Claim 18] A method of producing a formed article, the method comprising:
(a) optionally, a preheating step wherein a mold is heated at an elevated temperature;
(b) a coagulant application step wherein a coagulant composition is applied to a mold;
(c) an immersion step wherein a mold is immersed in a bath comprising the dip-molding composition of any one of claims 1 to 15;
(d) a vulcanization step wherein the mold is exposed to an elevated temperature; and

(e) a demolding step wherein the formed article is separated from the mold.

[Claim 19] The method of claim 18 comprising a preheating step wherein a mold is heated at a temperature of from about 80#°C to about 100#°C for a period of at least about 1 minute.

[Claim 20] The method of claim 18 or 19 wherein the coagulant composition comprises at least one coagulating agent selected from the group consisting of C₁ to C₆ alcohols, organic acids, and calcium chloride.

[Claim 21] The method of any one of claims 18 to 20 wherein the mold is immersed in a bath comprising the coagulant composition.

[Claim 22] The method of any one of claims 18 to 21 wherein the mold is immersed in a bath comprising the dip-molding composition for a period of at least about 10 seconds.

[Claim 23] The method of any one of claims 18 to 22 wherein the vulcanization step comprises heating the mold at a temperature of from about 80#°C to about 100#°C for a period of at least about 5 minutes.

[Claim 24] A method of producing a formed article, the method comprising:
(a) optionally, a preheating step wherein a mold is heated at an elevated temperature;
(b) a coagulant application step wherein a coagulant composition is applied to a mold;
(c) an immersion step wherein a mold is immersed in a bath comprising the dip-molding composition of any one of claims 1 to 15;
(d) a vulcanization step wherein the mold is exposed to ultraviolet radiation; and
(e) a demolding step wherein the formed article is separated from the mold.

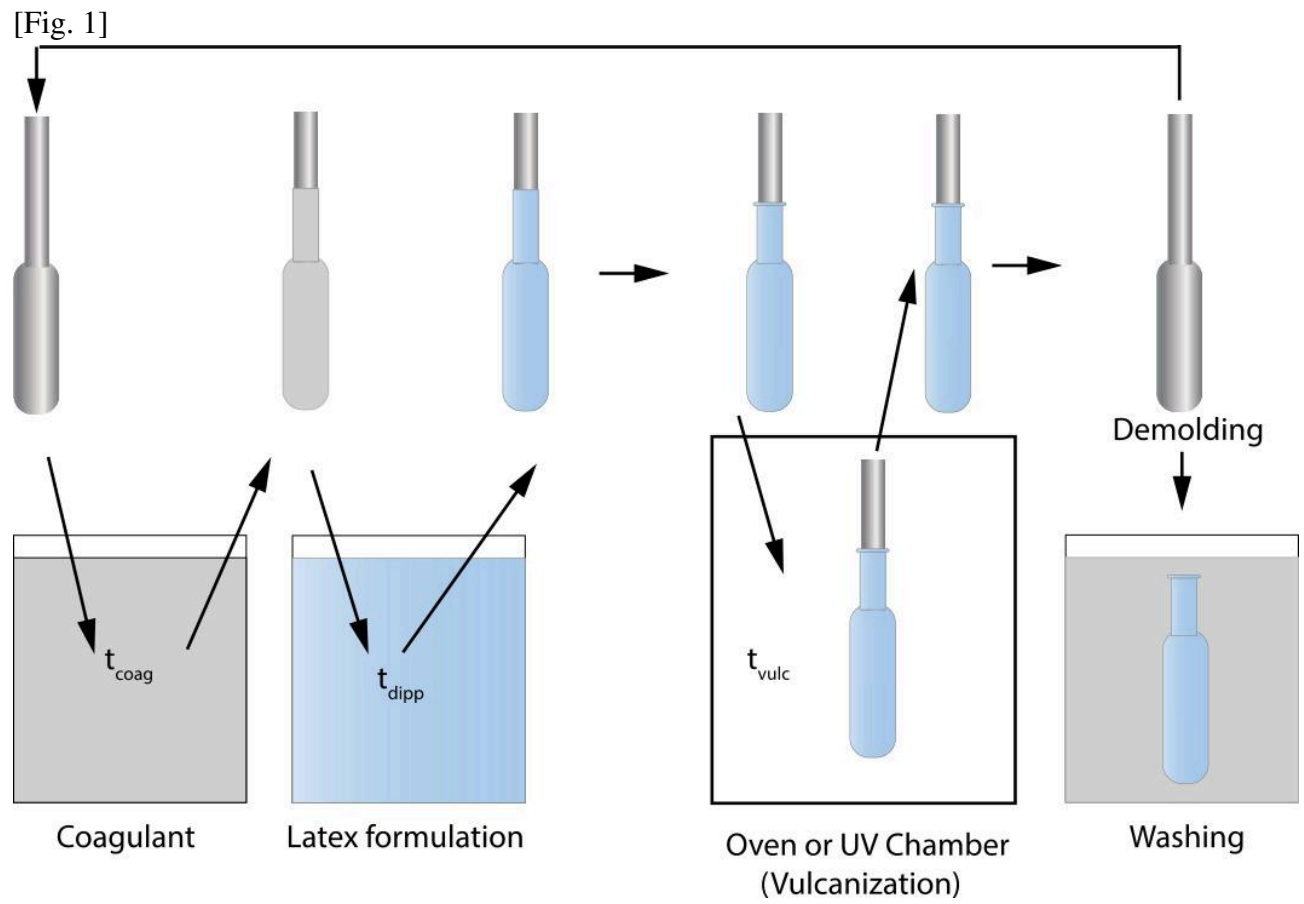
[Claim 25] The method of claim 24 comprising a preheating step wherein a mold is heated at a temperature of from about 80#°C to about 100#°C for a period of at least about 1 minute.

[Claim 26] The method of claim 24 or 25 wherein the coagulant composition comprises at least one coagulating agent selected from the group consisting of C₁ to C₆ alcohols, organic acids, and calcium chloride.

[Claim 27] The method of any one of claims 24 to 26 wherein the mold is immersed in a bath comprising the coagulant composition.

[Claim 28] The method of any one of claims 24 to 27 wherein the mold is immersed in a bath comprising the dip-molding composition for a period of at least about 10 seconds.

- [Claim 29] The method of any one of claims 24 to 28 wherein the vulcanization step comprises exposing the mold to ultraviolet radiation sufficient to impart at least 300 J/cm^2 to the surface of the mold.
- [Claim 30] A formed article produced by the method of any one of claims 18 to 29.
- [Claim 31] The formed article of claim 30, wherein said article is selected from the group consisting of elastomeric films, gloves, balloons and condoms.



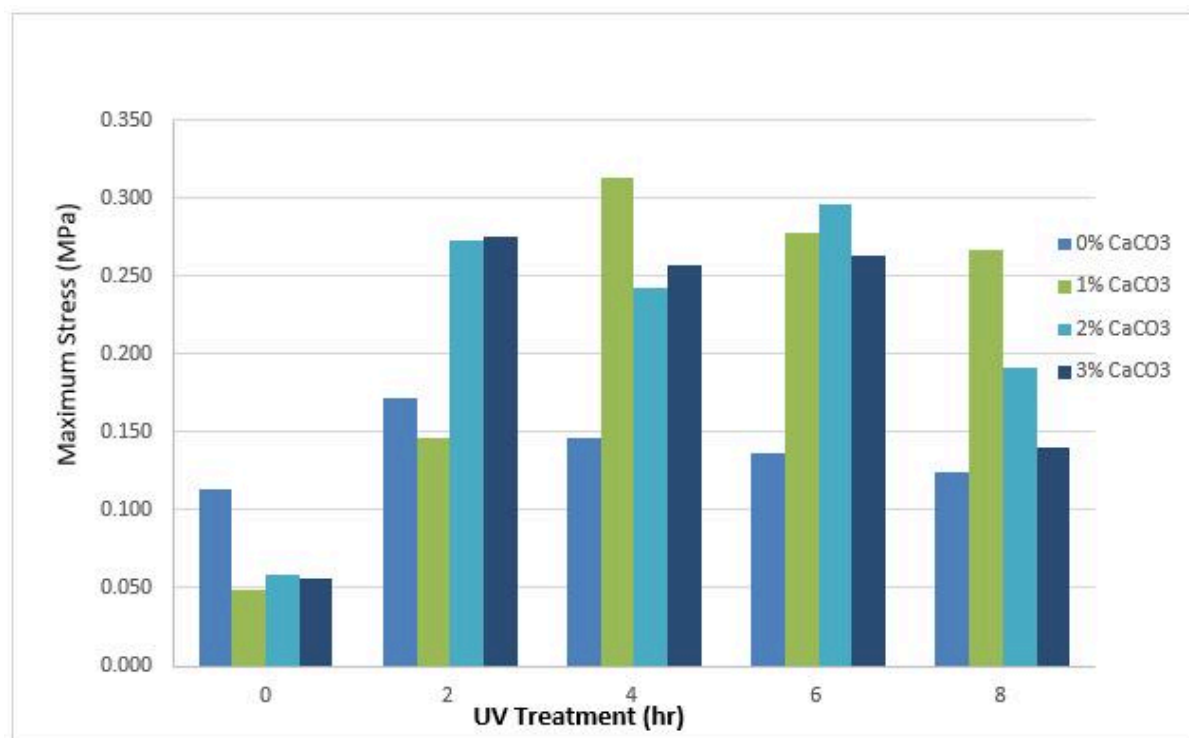
[Fig. 2]



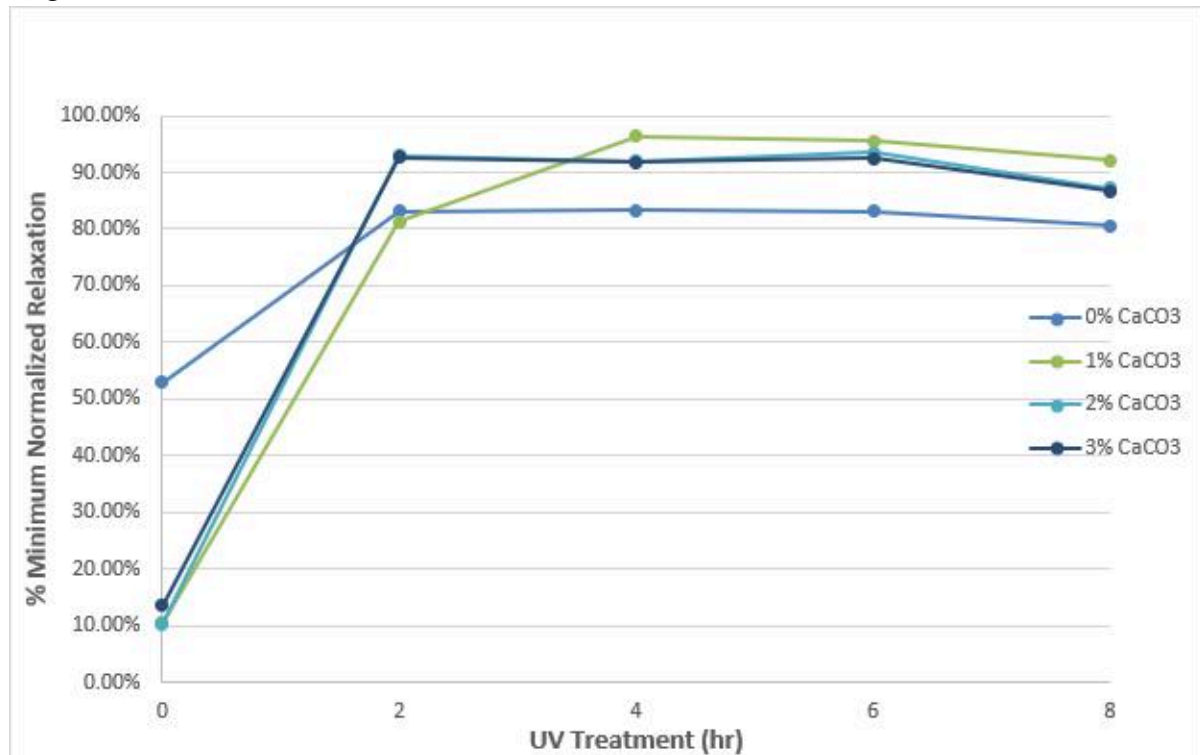
[Fig. 3]



[Fig. 4]



[Fig. 5]



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2025/052597

A. CLASSIFICATION OF SUBJECT MATTER INV. C08C1/06 C08K3/06 C08K5/357 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C08C C08K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO- Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 106 565 862 A (UNIV HAINAN) 19 April 2017 (2017-04-19) embodiments 2 and 3 -----	1 - 31
A	WO 2023/144631 A1 (AFLATEX TECH LDA [PT]) 3 August 2023 (2023-08-03) examples 1-7 -----	1 - 31
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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			CN 118946594 A	12-11-2024
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